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FORMULATION OF DDT SPRAYS AND DUSTS[1/]

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In connection with the intensive studies of the insecticidal properties of DDT (1-trichloro-2,2-bis(p-chlorophenyl)ethane), which have been made by many workers, methods of formulation of sprays and dusts have received much attention. Such experiments have been conducted largely under laboratory and small field-plot conditions.

Chemically pure DDT melts at 108.5°-109°C. Two grades of commercial product are available, one known as "technical DDT" specified to have a setting point not lower than 88°, and "DDT, purified," specified to have a melting point of at least 103°. The former has found use in louse powder, mosquito larvicide, and in general agricultural experimentation; the latter is intended for use in aerosol bombs.

DDT has been used in water suspensions, solutions, emulsions, dusts, and aerosols. The last-named have been discussed elsewhere, but the formulation of the other types of mixtures is presented in this paper.

WATER SUSPENSIONS

Water suspensions are divided into three classes - those resulting from the mixing of finely ground DDT (ground either dry or wet) with water, those resulting from the dilution with water of a solution of DDT in a water-miscible organic solvent, and those obtained by mixing diluents impregnated or coated with DDT with water.

[1/] This paper was read at the joint meetings of the American Association of Economic Entomologists and the Entomological Society of America at New York, N. Y., Dec. 13-14, 1944. Much of the information presented was obtained through correspondence with State experiment station investigators and from several Divisions of this Bureau.

Since technical DDT softens considerably below 88°C., and is not free flowing, it is necessary, when dry-grinding this compound, to mix it with a diluent such as calcite, talc, or pyrophyllite. Care must be exercised during grinding to avoid overheating the mill. Mixtures containing up to 50 percent of DDT may be prepared in this way. Mixtures of higher DDT content do not have desirable physical properties and are extremely difficult to grind.

Several commercial products containing various proportions of DDT, wetting agent, and diluent have been tested. One containing 10 percent of DDT has a surface mean particle diameter (determined by the air-permeation method, which does not necessarily reflect the particle size of the DDT) of 5 microns, as compared with 44 microns, the diameter of the openings in a U. S. No. 325 sieve. Another mixture containing 50 percent of DDT, which was micronized, had a surface mean particle diameter of 2.8 microns. Since DDT is known to be an effective contact insecticide, the use of small particles might be expected to give a more uniform distribution with a consequent improvement of insecticidal properties with certain insects. This is borne out by the increase in efficiency against larvae of the codling moth (Carpocapsa pomonella L.) when the particle size is 4 to 5 microns as compared with 8 to 9 microns. On the other hand, DDT deposits on glass plates have been observed to decrease in weight by an average of 5 to 10 percent during five successive 16-hour exposures to direct sunlight. Since rate of loss is directly related to the area of the exposed surface, extremely fine particles with their large specific areas may not be desirable if effectiveness over long periods of time in direct sunlight is required.

Mixtures containing as much as 10 percent of DDT with pyrophyllite can be wetted with water and under some conditions used as sprays. For general purposes, best results are obtained through the use of a surface-active agent to provide uniform wetting and dispersion of the DDT and adequate wetting of the sprayed surfaces without excessive run-off. Mixtures have been prepared by incorporating the surface-active agent before grinding. While this method has certain advantages with reference to ease of preparation, it has the disadvantage of making it impossible to vary the concentration of DDT without also changing the physical properties of the spray mixture and thus affecting the quantity of DDT deposited and the resistance of the residue to weathering. Since DDT studies are largely in the preliminary stage, both variables should be controlled by the investigator in order to insure a maximum of spray deposit and of distribution on specific types of foliage. This can be accomplished by the use of various amounts of surface-active agents.

The following wetting and sticking agents have been used with DDT-diluent mixtures: Soap powder, not to exceed 1 percent of the DDT; several proprietary compounds[2/] in amounts ranging from 0.1 to 0.5 percent of the DDT; materials of the nature of fish glue at the rate of 1 ounce, dissolved in 1 pint of water, per pound of DDT; and soybean flour at the rate of 1/2 pound per pound of DDT. In order to insure complete wetting of the DDT and to eliminate agglomerates, it is best to prepare a paste from the DDT-diluent mixture, the wetting agent, and enough water (about 1 1/2 pints per pound of mixture) to give a fairly heavy paste. This paste may be further diluted and added to the spray tank.

Several spray mixtures have been used which contain oil emulsions and DDT. Since DDT is preferentially wetted by oil, it is important to use the proper ratio of oil to DDT. If a large proportion of a quick-breaking emulsion is used, oil-coated DDT may collect on the surface of the spray mixture in curdy masses. One method of overcoming this difficulty consists in diluting the emulsion with a glue solution before adding the DDT. A formula consisting of 2 pounds of a 50:50 mixture of DDT and pyrophyllite or calcite, 1 quart of summer oil emulsion, 1 pint of fish-glue solution (prepared at the rate of 1 pound of semiliquid glue per gallon of water), and 100 gallons of water has been found to be satisfactory. The concentration of the fish-glue solution may be reduced to 1/4 pound per gallon of water.

Wet grinding is conducted in the usual manner in a ball mill. A wetting agent in the proportions previously mentioned in connection with dry-ground mixtures may be added previous to grinding. Mixtures prepared in this way have been reported to produce heavy spray deposits. They have the disadvantage common to paste products in that they tend to separate during storage.

DDT may be dissolved in water-miscible solvents such as methyl, ethyl, and isopropyl alcohols and acetone. When these solutions are poured into water, the DDT is thrown out of solution. The DDT dispersed from 1.5-percent solutions in the alcohols is finely divided and may be kept in suspension with moderate agitation. That dispersed from acetone solutions forms a gummy mass at first but later becomes crystalline.

2/These compounds include Orvus-WA (sodium salt of lauryl sulfate), Gardinol-WA (sodium salt of lauryl sulfate), Vatsol OS (sodium salt of an alkyl napthalenesulfonic acid), Tween 20 (a modified sorbitan monolaurate), Aresket (sodium monosulfonate of monobutyldiphenyl), and Ultrawet (water-soluble sodium sulfonate of petroleum hydrocarbons).

This objectionable feature may be overcome by adding a surface-active agent to the solution before mixing with water. One of the formulas used consists of 24 grams of DDT, 24 grams of Triton X-100 (polyethylene glycol phenylisooctyl ether), and acetone to make 100 ml., which is equivalent to 2 pounds of DDT per gallon of solution. On addition to water the DDT is dispersed as droplets of the gummy material mentioned above, which becomes crystalline and settles out in this form on standing. The extent to which the DDT is dispersed and the time required for crystallization and settling to take place are influenced by the proportion of surface-active agent in the acetone solution. Since this preparation is unstable, it should be used shortly after mixing and with moderate agitation.

SOLUTIONS

Solutions of DDT in organic solvents have been used for spraying the interiors of barns for the control of flies and for impregnating fabrics for the control of clothes moths. From 1 to 5 grams of DDT per 100 ml. of a petroleum fraction has been used for the first purpose, and a 1 percent solution of DDT in a volatile solvent such as xylene or acetone for the second. The solvent and concentration of DDT selected depend upon the insect to be controlled. Since technical DDT often contains some insoluble material, it may be necessary to filter the solution before use.

EMULSIONS

Emulsions of solutions of DDT in various solvents which are either substantially insoluble in water or only slightly soluble have been used by several investigators. In order to avoid precipitation, water-miscible solvents should not be used for this purpose. For the same reason, if the solvent is appreciably soluble in water, allowance should be made for this when diluting such emulsions. For example, emulsions of DDT-ethylene dichloride solutions have been used, but in some cases enough precipitate was deposited in the tank to clog the screen. To overcome this difficulty it would be necessary to adjust the concentrations of both materials in the emulsion to provide for enough ethylene dichloride to saturate the water plus the amount required to keep the DDT in solution.

Consideration should be given to the proportions and types of emulsifiers used. Since DDT is effective against many insects on contact, large proportions of the emulsifier may result in inferior control due to the coating of the DDT deposit by the emulsifier upon evaporation of the water and solvent. For this reason and also to prevent excessive run-off, it appears desirable to use only enough emulsifier to produce an emulsion which on dilution gives a spray with proper wetting qualities.

Some investigators have reported that emulsions are more effective for certain insects than suspensions, others have suggested that costs are excessive, and others have encountered difficulties as mentioned above.

Two types of emulsions have been used (1) those in which the DDT is dissolved in a volatile solvent, such as xylene, and (2) those in which the DDT is dissolved in a relatively nonvolatile solvent, such as petroleum oil. With the first type DDT crystals are distributed on the sprayed surface upon evaporation of the solvent, and with the second type the sprayed surface is coated with the solution on evaporation of the water.

Two formulas of the first type are as follows: (1) DDT 24 grams, Triton B-1956 (a phthalic glycerol alkyl resin) 3 grams, xylene to make 100 ml. (2) DDT 24 grams, Nacconal NRSF (sodium alkyl aryl sulfonate) 12 grams, Butyl Cellosolve (butyl ether of ethylene glycol) 10 ml., xylene to make 100 ml. These stock mixtures contain DDT at the rate of 2 pounds per gallon. They are best diluted to form emulsions by being added to 1 or 2 volumes of water, vigorously agitated, and then diluted with the remainder of the water.

An example of the second type is DDT 3 grams, mineral oil 75 ml., Gardinol-WA 1 gram, and water 25 ml. The DDT is dissolved in the oil, and this solution is emulsified on addition to a solution of the Gardinol-WA in the water stirring the mixture vigorously meanwhile. The volume of the product varies with the amount of air incorporated during emulsification. If the weight of DDT per gallon of spray mixture is to be controlled exactly, the dosage should be calculated on the basis of the volume of the product. The original proportions are equivalent to approximately 1/4 pound of DDT per gallon of emulsion. The solubility of DDT in 100 ml. of mineral oil at 27-30°C. (80-86°F.) ranges from 4 grams for Deobase (refined kerosene) to 10 grams for No. 2 fuel oil. Solubility in specific types or grades of oil at the minimum temperature to be encountered should be determined prior to emulsification. Emulsions of this type should be used soon after preparation.

Solvents other than those mentioned above, alone or in mixtures, as well as different proportions of the same or other surface-active agents, may be more desirable for the preparation of emulsions to be used for specific purposes. It is suggested that preliminary batches of spray mixtures be prepared and the physical properties observed before tests are made with insects.

DUSTS

Dust mixtures have, in general, been prepared by mixing diluents, such as pyrophyllite, talc, and walnut-shell flour, with finely ground DDT mixtures. Dusts containing as much as 10 percent of DDT are

sufficiently free-flowing for certain dusting purposes. On the other hand, dusts containing from 1 to 3 percent have better physical properties and have given good results. If the dust is prepared from a 50:50 mixture, care is required to obtain uniform distribution, as this mixture has a tendency to agglomerate in an ordinary dry mixer. Uniformity might be accomplished by passing it through a hammer mill or brushing through a series of screens.

Diluents such as pyrophyllite, talc, or walnut-shell flour may be coated or impregnated with DDT by dissolving it in a volatile solvent such as benzene or acetone, wetting the diluent with the solution, allowing the solvent to evaporate, and grinding the product. Fairly large batches may be prepared by spreading the diluent on a clean, hard surface and applying the DDT solution in successive portions from a sprinkling can. The mass should be remixed with a shovel after each sprinkling and then at intervals until all the solvent has evaporated. Only enough solvent should be used to dampen the diluent uniformly. Trial batches using the solvent without DDT will establish the proper proportions. The product should be ground to eliminate coarse agglomerates. A hammer mill is preferable for this purpose. Products containing more than 10 percent of DDT are liable to be difficult to grind.

Another method of impregnation used consisted in dissolving 2 pounds of DDT in 3 pounds of Velsicol AR-50 (alkylated naphthalenes) and impregnating 45 pounds of Pyrax ABB (pyrophyllite) with this solution in a ball mill. The resulting mixture was then added to another 50 pounds of Pyrax ABB and run through a brush mixer.

COMPATIBILITY

The compatibility of DDT with other insecticides, fungicides, and accessory materials has been studied from both the chemical and biological viewpoints. While DDT is a rather stable compound by itself, in alcoholic solution it readily reacts with alkalies with the loss of 1 mole of hydrochloric acid per mole of DDT and the formation of 1-dichloro-2,2-bis (p-chlorophenyl) ethylene. This compound, which is comparatively inert as an insecticide, is also formed at temperatures above the melting point of DDT in the presence of certain catalysts. Of the compounds which may be present in small amounts in accessory materials, iron and iron oxides, chromium, and anhydrous ferric, aluminum, and chromic chlorides are known to be active in this respect. Of this group the anhydrous chlorides are the most active. Ferric and chromic chlorides may be formed by the action of DDT on the metals themselves. Accessory materials such as kaolin, fuller's earth, bentonite, and some samples of talc and Pyrax ABB have shown definite catalytic activity. Other samples of talc and Pyrax ABB, as well as calcium oxide and hydrated lime, are substantially inactive.

Commercial grades of sodium fluoride, sodium fluosilicate, cryolite, paris green, calcium arsenate, and lead arsenate showed no catalytic action. With bordeaux mixture 0.04 mole, and with sulfur 0.07 mole of hydrochloric acid were obtained per mole of DDT. Pure nicotine, in common with strongly basic nitrogen-bearing compounds, reacts with DDT in the same manner as do alcoholic caustics.

Most of the solvents used with DDT tend to inhibit catalytic decomposition. The notable exceptions are naphthalene and the nitro- and chloro-benzenes. With p-dichlorobenzene the catalytic action of ferric chloride on DDT was shown to occur at room temperatures. Petroleum fractions, soybean oil, cyclohexanone, xylene, and Velsicol AR-60 (alkylated naphthalene) either completely or substantially inhibit the catalytic reaction of anhydrous ferric chloride.

While it has been shown that many compounds acting as catalysts at high temperatures will decompose DDT, it is possible that under field conditions decomposition may not take place or that the reaction may be so slow as to have little influence on insecticidal value of DDT. Apparently, however, spray mixtures containing only compounds which do not decompose DDT or which act as inhibitors in the laboratory would be most efficient under field conditions. Tests to determine the importance of these reactions under field conditions would be in order.

Biological tests have been made to determine the effectiveness of sprays containing DDT and other materials such as bordeaux mixture, sulfur, oil emulsions, Fermate (ferric dimethyl dithiocarbamate), and various accessory materials. These sprays have been used successfully with no injury to foliage except in a few cases where repeated applications were made. The addition of lime-sulfur, bordeaux mixture, and sulfur has been found to reduce the period of effectiveness. Whether this was due to decomposition to insecticidally inert compounds, or to the physical masking of the DDT in the deposits has not been established. Since DDT is a contact poison and its deposits are not permanent in direct sunlight, it is suggested that, in addition to normal mechanical loss, part of the decreased insecticidal value may be due to the loss of DDT from the surface of mixed deposits and the masking of the remainder within the deposits. Natural constituents, such as apple wax, may also influence insecticidal value.

DESIRABILITY OF A COMMON STANDARD OF COMPARISON

Considerable variation has been found in the results obtained with DDT in different parts of the country even when used to combat the same insect species. It is therefore very desirable to include in each set of tests against a given insect, material from a common source of the same formulation. In this way part of the variation in results would be eliminated or could be more readily interpreted.